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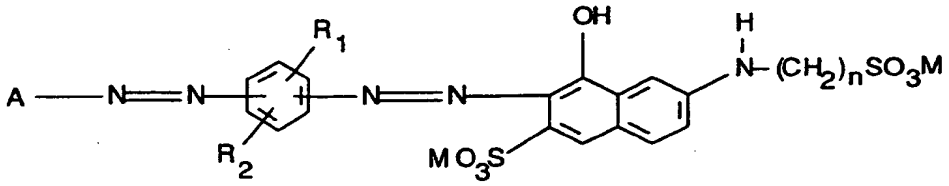
(71) Applicant: **ILFORD AG**
1701 Fribourg (CH)

(72) Inventor: **Peter, Heinz**
1700 Fribourg (CH)

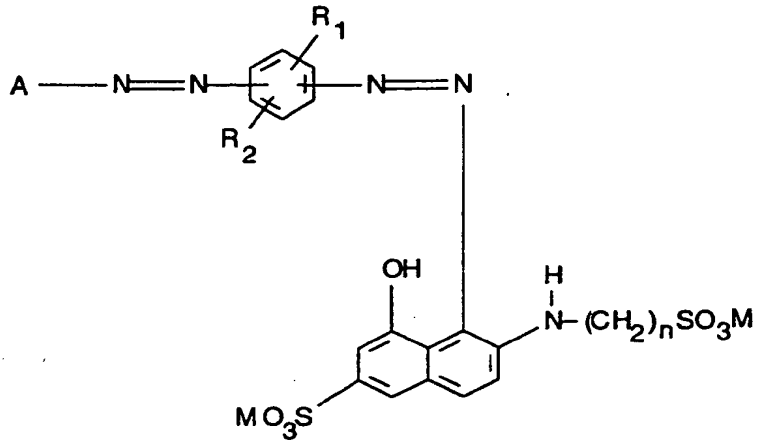
(54) Dyes for ink jet printing

(57) Disazo dyes of formula (VIII)



(VIII)

or of formula (IX)



(IX)

where A, R_1, R_2, n and M are as defined in the specification are excellent dyes for ink jet printing.

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Description

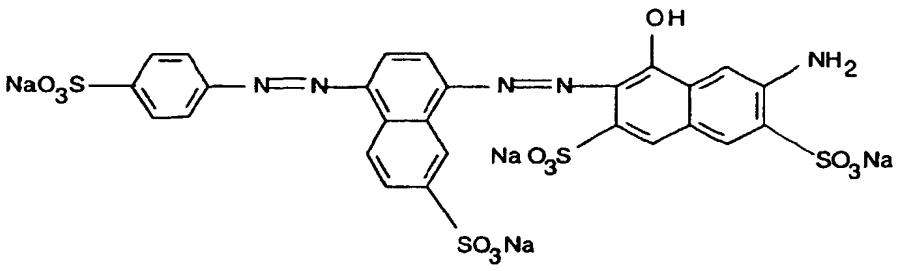
Field of the Invention

This invention relates to novel disazo dyes and to aqueous recording liquids comprising these dyes for ink jet printing processes.

Background of the Invention

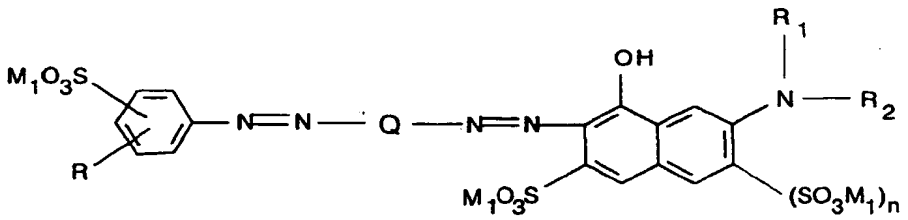
Ink jet printing systems generally are of two types: continuous stream or drop-on-demand. In continuous stream ink jet systems, ink is emitted in a continuous stream through an orifice or nozzle. The stream is perturbed, causing it to break up into droplets at a defined distance from the nozzle. At the break up point, the droplets are charged in accordance with digital data signals and passed through an electrostatic field which adjusts the trajectory of each droplet in order to direct it to a specific location on a recording medium or to a waste ink collecting recipient (e.g. for recirculation). In drop-on-demand systems, a droplet is expelled from a nozzle to a position on a recording medium in accordance with digital data. A droplet is not formed or expelled unless it is to be placed on the recording medium.
The most important part of an ink used in ink jet printing are the dyes. Although a number of dyes have been proposed none has been produced which meets all the requirements of a modern printing process.

C.I. Foodblack 2 (formula I) and dyes having similar structures have been mentioned as black dyes for ink jet inks in JP Patent Application 59-093'766. These dyes, however have a somewhat bluish hue and give images with poor light fastness.



(I) (C.I. Foodblack 2)

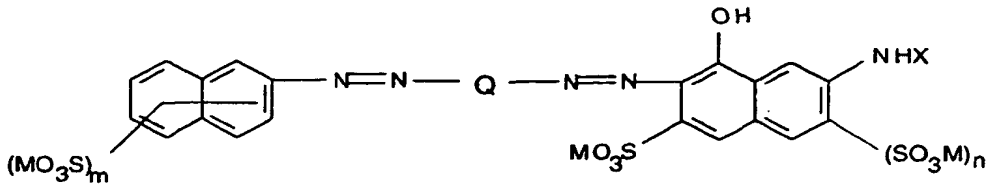
Black dyes of formula (II) or mixtures thereof have been described for example in US Patent 4'626'284



(II)

wherein Q represents a phenylene or naphthalene group substituted by a group shown by SO_3M_1; R represents a hydrogen atom, a lower alkyl group, a lower acylamino group, a nitro group or a halogen atom; R_1 represents a phenyl group substituted by a group shown by SO_3M_1 or a group shown by $COOM_1$, a lower alkyl group substituted by $COOM_1$, or a lower alkylaminocarbonyl lower alkyl group; R_2 represents a hydrogen atom, a lower alkyl group substituted by a group shown by $COOM_1$, or a lower alkylaminocarbonyl lower alkyl group; M_1 represents an alkali metal atom or an ammonium cation; and n represents 0 or 1.

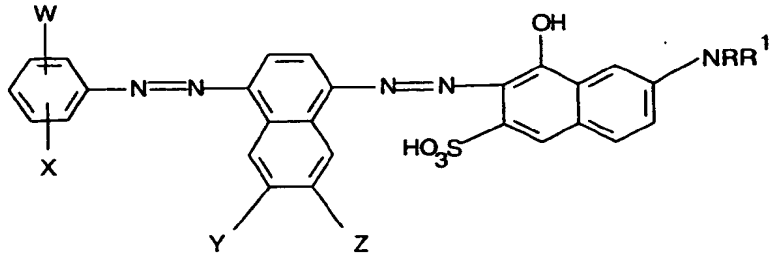
Black dyes of formula (III) or mixtures thereof have been described for example in US Patent 4'724'001



(III)

wherein Q represents a phenylene group substituted by a methyl group, a methoxy group or an ethoxy group or a naphthalene group substituted by SO_3M; X represents a hydrogen atom or a phenyl group substituted by SO_3M; m represents 1 or 2; n represents 1 when X represents a hydrogen atom and n represents 0 when X represents a phenyl group substituted by SO_3M, wherein X represents a hydrogen atom and m represents 1 when Q represents a naphthalene group substituted by SO_3M; and M represents an alkali metal atom or an ammonium cation.

Anionic black dyes of general formula (IV) are described in US Patent 5'053'495



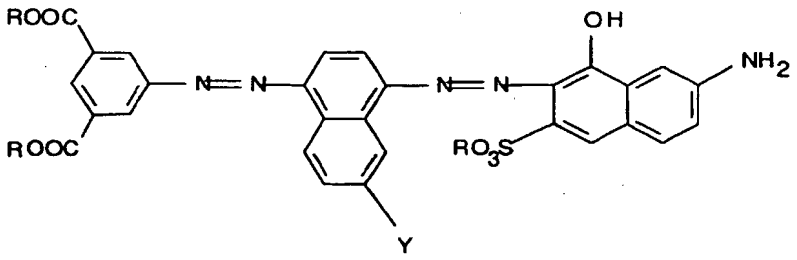
(IV)

where W is COOH; X is selected from the group consisting of hydrogen, COOH, SO_3H, halo, hydroxy, nitro, cyano, alkyl with 1 to 6 C atoms, alkoxy with 1 to 6 C atoms and acylamino with 1 to 6 C atoms; Y is hydrogen, COOH or SO_3H; Z is hydrogen, COOH or SO_3H, R and R^1 are independently hydrogen or alkyl from 1 to 6 C atoms substituted by 0, 1 or 2 $COOR^2$ groups; and R^2 is hydrogen or alkyl from 1 to 6 C atoms provided that there are at least two COOH groups and that the number of COOH groups is equal to or greater than the number of SO_3H groups.

These dyes are claimed to give differential water solubility depending upon pH. On a plain paper substrate with a pH from 5 to 7 the water solubility of these dyes is much lower than at higher pH and therefore the dyes will be more resistant to removal from the substrate by washing.

Such dyes, however, give rise to a poor smudge behaviour due to bronzing (association of the dye on the surface of the recording material). Although they can provide pure blacks on plain paper or coated paper, these dyes may provide a somewhat bluish hue on other recording media.

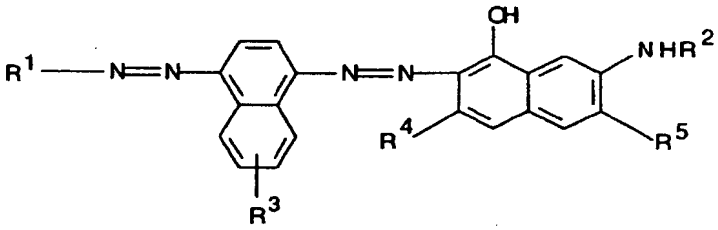
Black dyes with improved water fastness of general formula (V) have been described in EP Patent Application 0'612'820



(V)

where R is NH_4 and Y is hydrogen or SO_3R. These dyes, however, do not show a neutral hue and a yellow dye needs to be included in the black ink.

In EP Patent Application 0'597'672 black dyes of structure (VI) are described

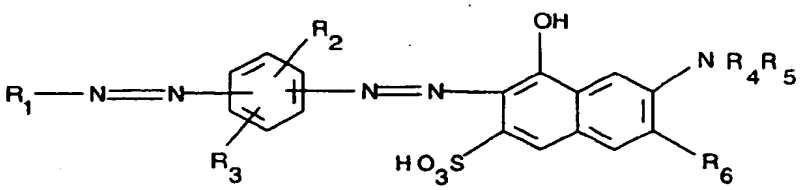


(VI)

where R^1 represents a phenyl or naphthyl group which may be substituted by a hydroxyl group, NH_2, SO_3M or COOM wherein M represents a hydrogen atom, or a cation species derived from an alkali metal, ammonia or an amine; R^2 represents a carboxyalkyl group wherein the carboxy group may form a salt with an alkali metal or ammonia, a substituted or unsubstituted alkoxyalkyl group or a substituted or unsubstituted phenyl or alkanoyl group, and R^3, R^4 and R^5, which may be the same or different, each independently represents a hydrogen atom or SO_3M wherein M is defined as above, provided that R^1 does not represent a phenyl group substituted with SO_3M when R^3, R^4 and R^5 all represent SO_3M. These dyes, however, do not show a neutral black hue and a yellow dye needs to be included in the black ink.

Of the compounds represented by the general formula (VI) wherein R^1 represents a phenyl group substituted by SO_3H and where R^3, R^4 and R^5 all represent SO_3H only a few dyes having particular structures can be combined with other dyes, because other combinations deteriorate the storage stability of the inks or the light fastness of the prints.

Black disazo dyes of formula (VII) are described in GB Patent Application 2'289'473 and WO Patent Application 95/31505



(VII)

wherein R_1 is optionally substituted phenyl or optionally substituted naphthyl; R_2 is hydrogen, halo, COOH, SO_3H, optionally substituted alkyl, optionally substituted alkoxy or optionally substituted alkylthio; R_3 is NR_7R_8; R_4 is hydrogen or optionally substituted alkyl; R_5 is hydrogen, optionally substituted alkyl or phenyl; R6 is hydrogen or SO_3H; R_7 is hydrogen or optionally substituted alkyl, R_8 is optionally substituted acyl.

Black disazo dyes of formula (VII) are described in JP Patent Application 07-268'256 where R_1 is optionally substituted phenyl, R_2 is branched alkyl or branched alkoxy with 1 to 8 C atoms; R_3 is alkoxy with 1 t0 9 C atoms; R_4 is hydrogen, optionally substituted phenyl, CH_2COOH or C_2H_4COOH; R_5 is hydrogen and R_6 is hydrogen or SO_3H.

Black disazo dyes of formula (VII) where R_1 is carboxyphenyl; R_2 and R_3 are hydrogen, methyl or methoxy; R_4 is hydrogen; R_5 is phenyl or carboxyphenyl and R_6 is hydrogen are described in JP Patent Application 04-304'274.

Black disazo dyes of formula (VII), where R_1 is optionally substituted carboxyphenyl; R_2 is alkyl or alkoxy with 1 to 4 C atoms or CH_2COOH; R_3 is alkoxy with 1 to 4 C atoms; R_4 is hydrogen; R_5 is hydrogen, alkyl with 1 to 4 C atoms or CH_2COOH and R_6 is hydrogen are described in US Patent 5'198'022. All these dyes are to be substituted by one or more carboxy or carboxy alkyl groups, preferably they contain at least as many COOH groups as SO_3H groups.

Dyes containing COOH groups however tend to cause "crusting" resulting in a "poor first ejection" according to EP Patent Application 0'612'820.

Dyes of the above mentioned structures considered to be state of the art do not satisfy all the required demands when used in aqueous inks for ink jet printing.

Dyes used for such recording liquids have to be sufficiently soluble, do not show bronzing on recording materials (association of the dye on the surface of the recording material), they have to be stable even when the recording liquid is stored for a long period of time, they need to provide printed images having high optical density, excellent water fastness and excellent light fastness.

Various types of compositions have been proposed as inks for use in ink jet printing. Typical inks are composed of various types of dyes, water, organic cosolvents and other additives.

In particular the inks have to meet the following criteria:

(1) The ink gives high quality images on any type of recording medium.
(2) The ink gives printed images exhibiting excellent water fastness.
(3) The ink gives printed images exhibiting excellent light fastness.
(4) The ink does not clog jetting nozzles even when these are kept uncapped while recording is suspended.
(5) The ink is quickly fixed onto recording media without bronzing and can not therefore be scrubbed off.
(6) The ink can be stored for a long period of time without deterioration in its performance.
(7) Physical properties of the inks, such as viscosity, conductivity and surface tension, are each within a defined range.
(8) The recording liquid has to be safe, non toxic and not flammable.

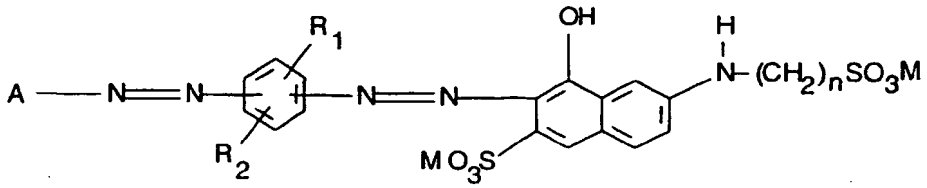
Reactive black dyes have also been proposed for ink jet printing for example in EP Patent Application 0'693'537. However, inks containing dyes with incorporated reactive groups deteriorate the storage stability of the inks and due to their potential health risk they are less suitable for handling in a non chemical environment.

Description of the Inventi n

This invention relates to novel black disazo dyes suitable for ink jet printing which provide images having neutral black colour, high optical density, high solubility, excellent Water fastness, excellent light stability and no or little association of the dye on the recording material (bronzing).

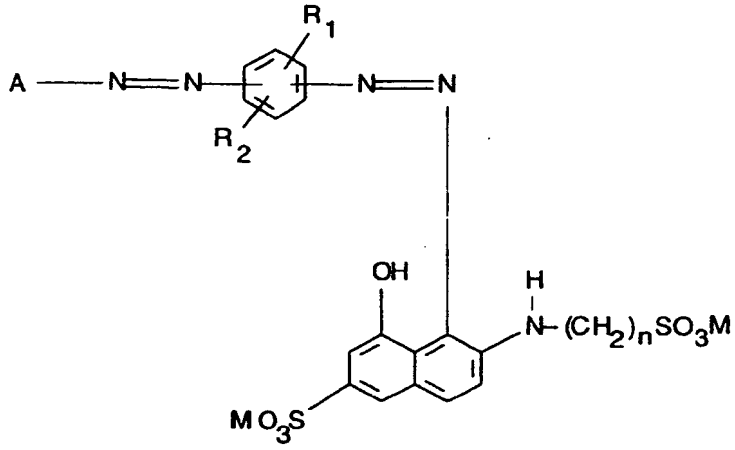
Another object of the present invention is to provide ink compositions for ink jet printing excellent in blackness on different ink receiving materials, such as plain papers, coated papers or sheets of synthetic material.
A further object of the present invention is to provide ink compositions satisfying all the requirements mentioned above.
Another object of the present invention is to provide black recording liquids which meets commercial requirements.

According to a first aspect of the present invention there are provided new black dyes of formula (VIII)



(VIII)

or formula (IX)



(IX)

wherein

A is optionally substituted phenyl or optionally substituted naphthyl;
R_1 is hydrogen, alkyl, optionally substituted alkyl, alkoxy, optionally substituted alkoxy, thioalkoxy, optionally substituted thioalkoxy, halo, COOM or SO_3M;
R_2 is alkyl, optionally substituted alkyl, alkoxy or optionally substituted alkoxy;
n is 2 to 4;
and
M is hydrogen, a metal atom, preferentially an alkali metal atom, ammonium or ammonium substituted with alkyl, alkoxyalkyl or hydroxyalkyl each having 1 to 12 C atoms.

When A is substituted phenyl it preferably carries from one to three substituents selected from sulpho, carboxy, carboxamido, N-substituted carboxamido as for example N-carboxymethylcarboxamido or N-(2-adipyl)-carboxamido; alkyl with 1 to 18 C atoms, preferably with 1 to 4 C atoms, substituted alkyl as for example hydroxymethyl, carboxymethyl, sulphomethyl, phosphonomethyl, hydroxyethyl, carboxyethyl, cyanoethyl, 4-carboxybutyl; halogen, hydroxy, cyano, alkoxy with 1 to 18 C atoms, preferably with 1 to 4 C atoms; substituted alkoxy as for example 2-hydroxyethyloxy or ω-

sulphoalkoxy; alkylthio, substituted alkylthio as for example ω-sulphoethylthio or ω-sulphopropylthio. It is still more preferred that when A is substituted phenyl one of its substituents is sulpho or carboxy and one or two substituents are selected from hydrogen, chloro, hydroxy, alkoxy or carboxy.

When A is substituted naphthyl it preferably carries from one to three substituents selected from sulpho , carboxy or hydroxy. It is preferred that the naphthyl is substituted by one to three sulpho groups, more preferably by one or two sulpho groups.

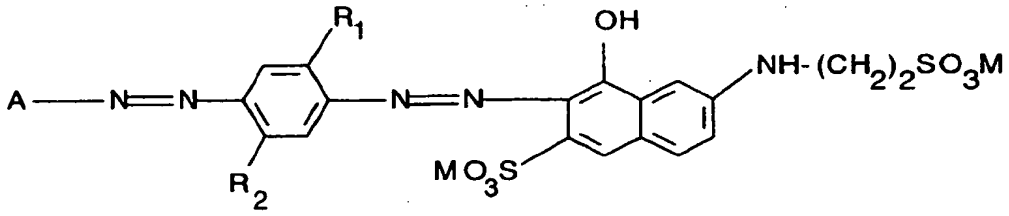
When R_2 is alkyl R_1 is hydrogen, alkyl, alkoxy or substituted alkoxy as for example 2-hydroxyethoxy, ω-sulphoalkoxy, 2-hydroxy-3-sulphopropoxy; alkylthio or substituted alkylthio as for example 3-sulphopropylthio; sulpho or carboxy.

The compounds of formulas (VIII) and (IX) may be in the free acid form or an inorganic or organic salt thereof. They are preferably in the form of their salts with cations such as alkali metal, ammonium or optionally substituted ammonium or mixtures of such cations.

In a preferred embodiment of the invention the compounds of formulas (XIII) and (IX) the two azo groups are in para relationship across the central phenylene group and R_1 is also in para position to R_2. It is also preferred that R_2 is ortho to the azo group linking A to the central phenylene moiety.

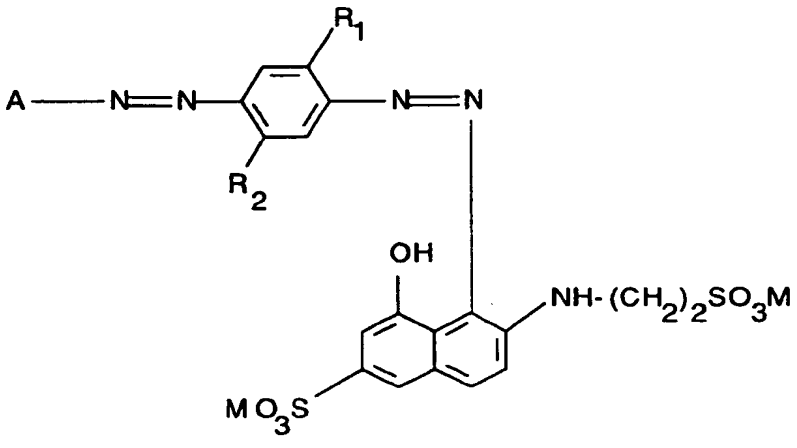
It is further preferred that the compounds of formulas (VIII) and (IX) have at least as many sulpho groups as carboxy groups, preferably more sulpho groups than carboxy groups and that n is equal to 2.

Especially preferred are compounds of Formula (X)



(X)

and formula (XI)



(XI)

wherein the substituents are as described above.

The compounds of formulas (X) and (XI) may be in the free acid form or in the form of inorganic or organic salts

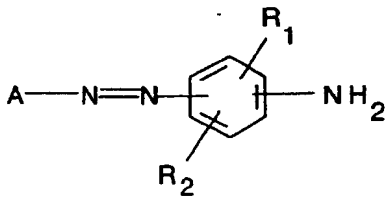
thereof, but they are preferably in the form of their salts with cations such as alkali metal, ammonium or optionally substituted ammonium or mixtures of such cations. Examples of substituted ammonium cations include 2-hydroxyethylammonium, bis-(2-hydroxyethyl)-ammonium, tris-(2-hydroxyethyl)-ammonium, bis-(2-hydroxyethyl)-methyl-ammonium, tris-[2-(2-methoxyethoxy)-ethyl]-ammonium, 8-hydroxy-3,6-dioxaoctylammonium and tetraalkylammonium as for example tetramethylammonium or tetrabutylammonium.

It is to be understood that the present invention covers all tautomeric forms of the compounds of formulas (VIII), (IX), (X) and (XI).

The present invention relates not only to compounds of formulas (VIII), (IX), (X) and (XI), but also to mixtures comprising two or more compounds of formulas (VIII), (IX), (X) and (XI).

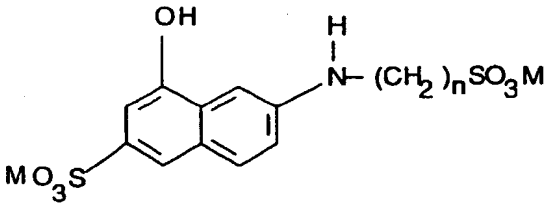
Dye Synthesis

The compounds according to formulas (VIII), (IX), (X) and (XI) may be prepared by methods known in the art by diazotising an amine of formula (XII)



(XII)

and subsequent coupling with a compound of formula (XIII)



(XIII)

For example compounds of formula (XII) may be prepared by diazotising an amine of formula A-NH_2, preferably below 5° C, with nitrite and mineral acid, and subsequent coupling with an aniline substituted by R_1 and R_2.

The compounds of formulas (VIII), (IX), (X), (XI) and (XII) may be prepared by methods described, for example, in GB Patent Application 2'289'473 or by methods similar thereto.

Compounds of formula (XIII) may be prepared using the Bucherer reaction in which 1-hydroxy-3-sulpho-7-hydroxy (or 7-amino)-naphthalene is reacted with an amine $NH_2(CH_2)_nSO_3M$ in the presence of an alkali metal or ammonium sulphite and / or bisulphite with heating, preferably at a temperature of from 60° C to 100° C.

The present invention will be illustrated in more detail by the following examples without limiting the scope of the claimed structures in any way.

Ink Composition

Compounds or mixtures of compounds represented by formulas (VIII), (IX), (X) and (XI) are useful colorants for the preparation of black recording liquids for ink jet printing.

A suitable ink comprises one or more compounds according to the present invention and a liquid aqueous medium. The

ink preferably contains from 0,5% to 20%, preferably from 0,5% to 5% by weight of the compound or compounds, based on the total weight of the ink. The liquid medium is preferably water or a mixture comprising water and water soluble or water miscible organic solvents or mixtures thereof. Examples of suitable ink media are given for example in US Patents 4'626'284, 4'703'113, 4'963'189, GB Patent Application 2'289'473 and EP Patent Applications 0'425'150 and 0'597'672.

Examples

Prepared compounds of formula (X) are listed in Table 1.

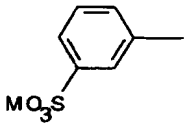
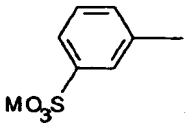
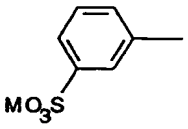
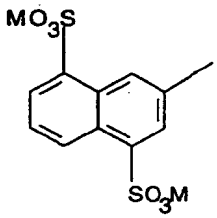
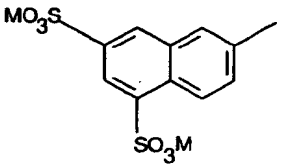
Compound No.	A	R_1	R_2	M
1		$-OCH_3$	$-CH_3$	Na
2		$-OCH_2CH_2OH$	$-CH_3$	Na
3		$-OCH_3$	$-OCH_3$	Na
4		$-OCH_3$	$-CH_3$	Na
5		$-OCH_2CH_2OH$	$-CH_3$	Na
6		$-OCH_3$	$-CH_3$	Na
7		$-OCH_3$	$-OCH_3$	Na

Table 1

A prepared compound of formula (XI) is listed in Table 2.

Compound No.	A	R_1	R_2	M
8		$-OCH_3$	$-CH_3$	Na

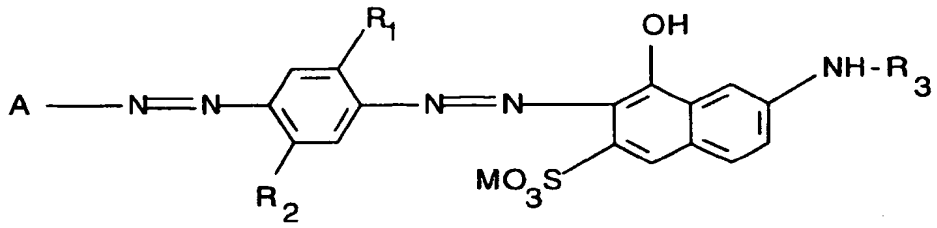
Table 2

A prepared mixture of compounds of formulas (X) and (XI is listed in Table 3.

Compound No.	A	R_1	R_2	M
9	 1 : 1 mixture of compounds 4 and 8	$-OCH_3$	$-CH_3$	Na

Table 3

Previously known disazo dyes according to general formula (XIV)



(XIV)

are listed in Table 4.

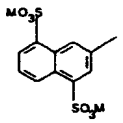
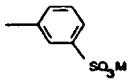
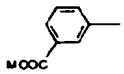
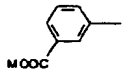
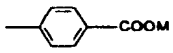
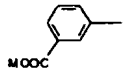
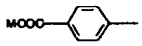
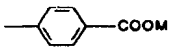
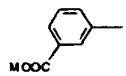
Compound No.	A	R_1	R_2	R_3
10		-H	$-CH_3$	
11		$-OCH_3$	$-NHCOCH_3$	-H
12		$-OCH_3$	$-NHCOCH_3$	
13		$-OCH_3$	$-NHCOCH_3$	$-CH_2CH_2COOM$
14		$-OCH_3$	$-OCH_3$	
15		$-OCH_3$	$-CH_3$	-H

Table 4

Evaluation Tests

Preparation Example of Inks

The present invention in so far as it relates to inks is further illustrated by using dyes described in Tables 1, 2 and 3. 100 g of each ink were prepared by heating the dye (3-7 g), 5g of glycerol, 1.1 g of tetraethyleneglycole and 1.2g of a biocide solution (Promexal X50, available from Zeneca, Manchester, England) together with water to a temperature of approximately 50° C under stirring for one hour to make a solution, cooling it down to 20° C, adjusting pH to 7.5 and passing the solution through a Millipore filter of 0.5 μm pore diameter. The dye quantity was adjusted in a way that the printed density was the same for all dyes.

Application Example of Inks

An ink receiving sheet for the testing procedures was prepared in the following way:
30 g gelatine with a high isoelectric point (type St 70'810, available from Deutsche Gelatinefabriken, Eberbach, Germany) were dissolved in 360 ml of deionised water. To this solution was added 1 g of a surfactant (Olin 10G, available from Olin Corporation, Norwalk, USA). Immediately before coating 6.6 g of a 3% solution of 2-(4-dimethyl-carbamoyl-pyridino)-ethane-sulfonate was added and the pH was adjusted to 6.5. 100 g/m^2 of this solution was then coated onto an RC paper support using a barcoater. The sheets were dried for 12 hours.

The inks were then jetted onto these receiving sheets with an HP560 ink jet printer to evaluate their printing performance. The evaluation methods for (A) dye solubility, (B) colour co-ordinates, (C) smudge resistance and (D) light fastness are as follows:

(A) **Dye Solubility**

The dye was dispersed or solubilised in deionised water and the dispersion or solution was stirred for one hour at 50° C. Then the mixture was cooled down to 20° C, centrifuged and filtered. The solubility of the dye was calculated a)

from UV / VIS spectral data of the mother liquor (solution) or b) based on the dried filter residue.

(B) **Colour Co-ordinates**

L*a*b*-values were measured on printed samples using a Gretag SPM 100 spectrometer, available from Gretag AG, Regensdorf, Switzerland.

(C) **Smudge Resistance**

The smudge behaviour was evaluated by determining the degree of smear of the dye in images printed as described above according to the following criteria:

⊕ : Little or no smear
◊ : Slight smear
Ø : Severe smear

(D) **Light Stability**

The printed samples were irradiated in an Atlas Ci35A Weather-O-Mete® with a 6500 W Xenon lamp until a total illumination of 20 kJoule/cm^2 was reached. The loss of density was measured with an X-Rite® densitometer and is expressed in % loss of initial density.

The solubilities of the dyes determined as described above are shown in Table 5.

Table 5

Dye No.	Solubility (in g per 100 ml)
2	> 20
4	> 20
6	> 20
12	3.6
14	17

The dyes 2, 4 and 6 according to the present invention show a much higher solubility than the previously known black disazo dyes 12 and 14.

The absorption maxima and the results of the tests (B) to (D) are reported in Table 6 for the dyes of the invention and the comparative values for previously known disazo dyes in Table 7.

Table 6

Compound No.	λ_{max} in water (nm)	L*a*b*-Value	Smudge Value	Loss of Density in %
1	569	10,0 / 13,6 / -0,8	⊕	6
4	584	2,4 / 3,8 / -0,9	⊕	3
5	583	2,6 / 2,4 / -0,4	⊕	3,3
6	575	15,5 / 5,1 / 0,7	⊕	5
7	595/491	5,8 / 4,3 / 0,7	◊	7
9	580	2,2 / 2,0 / 0,1	⊕	4,2

Table 7

Compound No.	λ_{max} in water (nm)	L*a*b*-Value	Smudge Value	Loss of Density in %
10	559	4,1 / 13,0 / 2,9	⊕	8,6
11	557	20,6 / 7,5 / -1,1	Ø	Bronzing
12	498	13,2 / 4,6 / -3,3	◊	10,3
13	488	2,2 / 1,3 / 1,1	Ø	Bronzing
14	584	11,1 / 8,1 / -5,0	Ø	10,6
15	557	12,9 / 8,1 / 4,0	Ø	Bronzing

For black dyes to have a neutral hue, a^* and b^* values have to be zero. A comparison of the measured colour co-ordinates of printed samples with inks made with dyes of the present invention (Table 6) shows clearly that these dyes give more neutral blacks than samples printed with inks using previously known disazo dyes (Table 7).

As is clearly demonstrated, the previously known black disazo dyes tend to severe smear and bronzing, whereas the dyes or mixtures of dyes according to the present invention show an excellent smudge resistance and no or very low bronzing.

As is clearly shown, the dyes of the present invention (Table 6) show significantly smaller losses in density after exposure to 20 kJoule/cm^2 compared to dyes of the prior art (Table 7).

Comparative results were also obtained with the commercially available black inks for the HP 560 and Lexmark 4076 printers. The results for these inks are listed in Table 8.

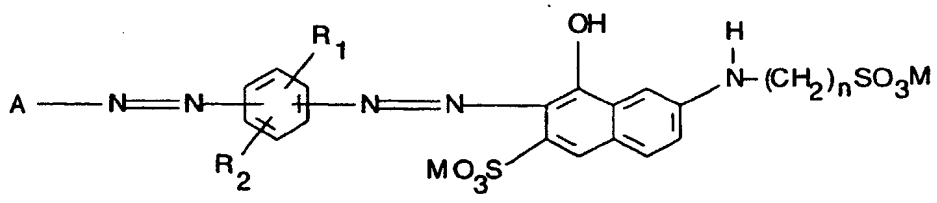
Table 8

Compound No.	L*a*b*-Value	Smudge Value	Loss of Density in %
Hewlett-Packard 560 Black	4,7 / 7,3 / -5,5	⊕	8,9
Lexmark 4076 Black	4,2 / 5,7 / -1,0	◊	12,6

As reflected by the measured values the light fastness of the dyes according to the present invention (Table 6) is markedly improved compared to dyes in commercially available black inks (Table 8).

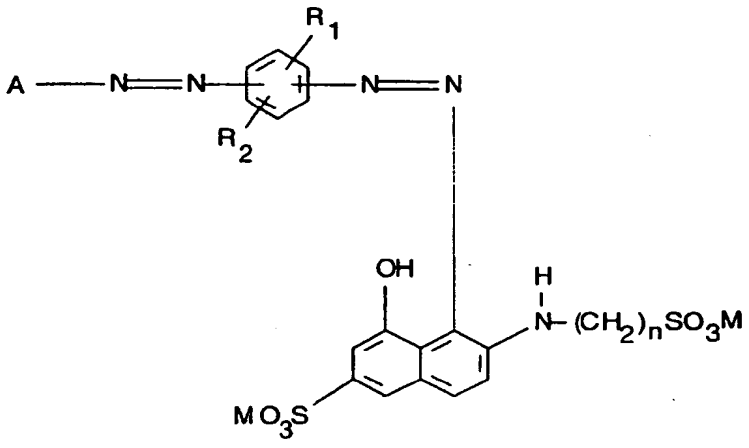
Claims

1. A disazo dye of formula (VIII)



(VIII)

or of formula (IX)



(IX)

wherein

A is optionally substituted phenyl or optionally substituted naphthyl;
R_1 is hydrogen, alkyl, optionally substituted alkyl, alkoxy, optionally substituted alkoxy, alkylthio, optionally substituted alkylthio, halo, COOM or SO_3M;
R_2 is alkyl, optionally substituted alkyl, alkoxy or optionally substituted alkoxy;
n is 2 to 4;
and
M is hydrogen an alkali metal atom, ammonium or ammonium substituted with alkyl, alkoxyalkyl or hydroxyalkyl each having 1 to 12 C atoms.

2. A disazo dye according to claim 1 wherein

A is substituted phenyl with one to three substituents selected from the group consisting of sulpho, carboxy, carboxamido, N-substituted carboxamido; alkyl with 1 to 18 C atoms, substituted alkyl; halogen, hydroxy, cyano, alkoxy with 1 to 18 C atoms, substituted alkoxy; alkylthio, substituted alkylthio.

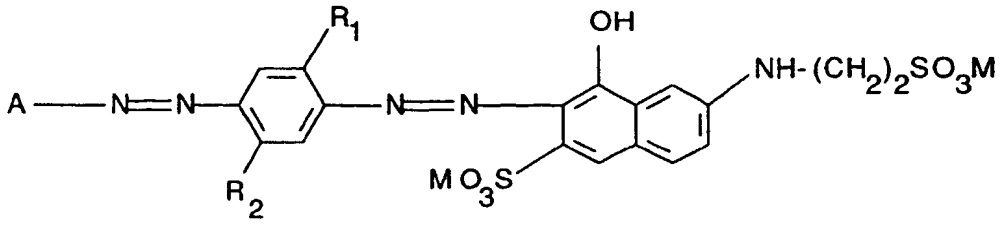
3. A disazo dye according to claim 2

where A has one sulpho or carboxy substituent and one or two further substituents are selected from the group consisting of hydrogen, chloro, hydroxy or carboxy.

4. A disazo dye according to claim 1 wherein

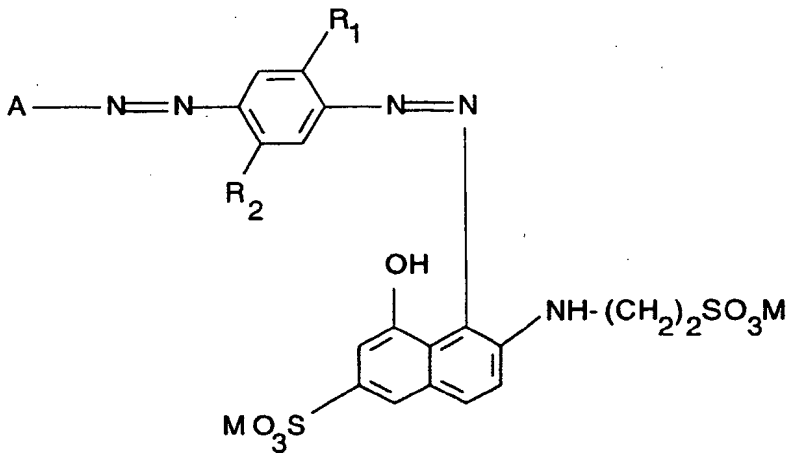
A is substituted naphthyl with from one to three substituents selected from sulpho, carboxy or hydroxy.

5. A disazo dye of formula (X)



(X)

or formula (XI)



(XI)

wherein

A is optionally substituted phenyl or optionally substituted naphthyl;

R_1 is hydrogen, alkyl, optionally substituted alkyl, alkoxy, optionally substituted alkoxy, alkylthio, optionally substituted alkylthio, halo, COOM or SO_3M;

R_2 is alkyl, optionally substituted alkyl, alkoxy or optionally substituted alkoxy;

and

M is hydrogen, a metal atom, preferentially an alkali metal atom, ammonium or ammonium substituted with alkyl, alkoxyalkyl or hydroxyalkyl each having 1 to 12 C atoms.

6. A disazo dye according to claim 5 wherein

A is as defined in claim 2.

7. A disazo dye according to claim 5 wherein

A is as defined in claim 3.

8. A disazo dye according to claim 5 wherein

   A is as defined in claim 4.

9. An ink for ink jet printing comprising a dye or a mixture of dyes as claimed in anyone of claims 1 to 8.

10. An ink for ink jet printing which contains in addition to a dye or dyes as claimed in anyone of claims 1 to 8 one ore more other dyes.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 2274

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A D	DE 36 16 128 A (CANON KK ;MITSUBISHI CHEM IND (JP)) 20 November 1986 * Compound no 6; preparation example 3; claims * & US 4 724 001 A	1-10	C09B31/08 C09D11/00 //C09B67/22
A,D	GB 2 289 473 A (ZENECA LTD) 22 November 1995 * claims; examples 1,9 *	1-10	
A,D	US 5 198 022 A (AULICK RODNEY O ET AL) 30 March 1993 * claims; example 3 *	1-10	
A,D	PATENT ABSTRACTS OF JAPAN vol. 017, no. 124 (C-1035), 16 March 1993 & JP 04 304274 A (MITSUBISHI KASEI CORP), 27 October 1992, * abstract; example 1 *	1-10	
A D	DE 34 36 891 A (CANON KK ;MITSUBISHI CHEM IND (JP)) 25 April 1985 * table 1, compounds 21, 23 * & US 4 626 284 A	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C09B C09D
A,D	WO 95 31505 A (ZENECA LTD ;KENYON RONALD WYNFORD (GB); GREGORY PETER (GB)) 23 November 1995 * claims; examples *	1-10	
A	CH 635 361 A (SANDOZ AG) 31 March 1983 * examples *	1-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 June 1997	Ginoux, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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